



Short communication

X-ray evaluation of the boundary between polymer electrolyte and platinum and carbon functionalization to conduct protons in polymer electrolyte fuel cells



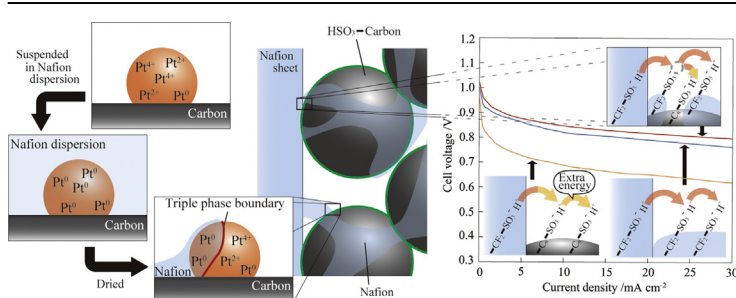
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HIGHLIGHTS

- Boundary between proton conducting polymer and Pt surface was evaluated by synchrotron X-rays.
- The boundary in PEFC catalyst was monitored based on the electronic state of Pt sites.
- Proton conductivity increased by functionalizing sulfonate/sulfate groups over carbon black.
- Functionalized sulfonate/sulfates on C were proton conductive on a similar level to Nafion.
- Functionalized sulfonate/sulfates on C were energetically inferior to sulfonates of Nafion.

GRAPHICAL ABSTRACT



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ABSTRACT

In polymer electrolyte fuel cells (PEFCs), it is important to secure proximate diffusion paths of reactants and electrons. One approach is to optimize the boundary between polymer electrolyte and Pt nanoparticle surface. Based on synchrotron X-ray absorption fine structure to monitor directly the status of catalysts in PEFCs, it was found that Pt sites were reduced to Pt^0 by alcohols contained in polymer electrolyte dispersion solution during the preparation of cathode of PEFC. As in membrane electrolyte assembly, only the Pt sites not covered by polymer electrolyte re-oxidized to $\text{Pt}^{2+/4+}$. Thus, the interface between Pt and polymer electrolyte was evaluated. The other approach is to functionalize carbon surface with sulfonate/sulfate group to conduct protons. Similar level of proton conductivity was observed in current–voltage dependence compared to using polymer electrolyte, but polymer electrolyte was advantageous to lose less voltage for activation. Based on this comparison, optimum catalyst on cathode is proposed comprising surface sulfonate/sulfate group on carbon mixed with polymer electrolyte. Further optimization of cathode catalyst is proposed to functionalize carbon with sulfonate group linked to fluorocarbon branch.

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1. Introduction

In polymer electrolyte fuel cells (PEFCs), active site exists at the triple phase boundary in the catalysts [1]. The solid, liquid, and gas phases play the roles of electron conduction, proton diffusion, and

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reactant gas diffusion, respectively. However, coincidence of the three factors depends on luck during preparation conditions of membrane electrolyte assembly (MEA), and triple phase boundary is in general very limited as points. Thus, it is important to extend the two-phase boundary from line to face to maximize the number of active sites of PEFC at the triple phase boundary.

First approach is to evaluate the boundary between active platinum nanoparticles and proton-conducting polymer. Epting et al. observed Pt particle agglomeration and the pore spaces in the Pt/C catalyst layer using 3-dimensional transmission electron microscope (TEM) [2]. This was a direct evaluation of reactant diffusion path. However, it is still a difficult task to evaluate how much the surface of metal nanoparticle is covered with light, soft constituent, e.g. polymer electrolyte. In this study, the boundary formation between Pt nanoparticles and proton conducting polymer was monitored as the electronic state change of Pt sites by Pt L₃-edge X-ray absorption fine structure (XAFS). The electronic state is quite sensitive to the surrounding environment, i.e. proton conducting polymer and oxidative/reductive gas. Pt L₃-edge XAFS was recently applied to probe one monolayer of Pt over Rh(111) crystal applied by 0–1.6 V [3].

Second approach is to maximize the boundary between electron conducting carbon (C) and proton conducting medium. The approach in this study is to functionalize the surface of electron conducting C to conduct also protons. C functionalization by sulfonate/sulfate group was reported for solid Brønsted acid catalysts [4–7]. The point-like triple phase boundary was expected to extend to line-like using functionalized C material to conduct both electrons and protons in PEFC electrodes.

2. Experimental

2.1. Electronic state measurements of platinum in replica Pt–C catalyst

The replica Pt–C catalyst was prepared following the procedure reported in ref. 8. In brief, Pt(NH₃)₄(OH)₂ was ion-exchanged with Al–MCM-41 (Al₂O₃:SiO₂ molar ratio = 1:79, 1.11 wt% Al; Aldrich) at 353 K for 48 h. Obtained white powder was heated at 573 K in H₂ and then at 973 K in the flow of ethyne and nitrogen at a rate of 200 mL min^{−1} with the ratio of 1:9. Next, Al–MCM-41 template was removed by washing with 15% HF aqueous solution to obtain replica Pt–C powder. Similar synthesis route to this replica Pt–C was also reported using SBA-15 as a template for Pt–C [9] and Pt/Ru–C [10].

50 mg of above obtained replica Pt–C powder (6.1 wt% of Pt; mean Pt particle size 2.0 nm) was suspended in 0.2 mL of Nafion dispersion solution [diluted to 2.8–1.5% by mixing 5% solution (DE521, Wako Pure Chemical) with ethanol] and dried (replica Pt–C–Nafion). Separately, replica Pt–C sample was immersed in 0.2 mL of ethanol and dried. Pt supported on Ketjen C black (EC300J) was provided from Ishifuku Metal Industry (IFPC40-II; 39.5 wt% Pt, mean Pt particle size 4.5 nm). Pt L₃-edge XAFS spectra were measured at 290 K in transmission mode in the Photon Factory at the High Energy Accelerator Research Organization (KEK, Tsukuba) on the beamlines of 7 C, 9 C, and 12 C [8,11]. The storage ring energy was 2.5 GeV and the current was 180–450 mA. Si(111) double crystal monochromator was used. The data were analyzed using the software package XDAP [12].

2.2. C functionalization with sulfonate/sulfate group

Five types of C powder samples (Ketjen black EC300J, Vulcan XC72R, Darco G-60, Norit SX-Plus, and Norit SX-II) were used as received. 1 g of C powder was mixed with 50 mL of fuming sulfuric

acid (15% of free SO₃). The suspension was heated at 313–363 K for 10 h in flask equipped with a reflux condenser. Then, the suspension was filtered by a polytetrafluoroethylene (PTFE)-based membrane filter (Omnipore JGWP04700, Millipore) with a pore size of 0.2 μm and washed with hot water (353 K) until the pH of filtrate increased to 6.0. All the procedures were performed under argon atmosphere. Thus-obtained powder is denoted as HSO₃–C (precursor C powder name). The proton contents in HSO₃–C were determined by reverse titration. Namely, slightly excessive sodium hydroxide solution (10 mmol L^{−1}) was added to HSO₃–C powder than to neutralize and well mixed using ultrasonic. The suspension was filtered using a PTFE-based membrane filter (Omnipore JGWP04700). The amount of excessive sodium hydroxide in the filtrate was determined by the titration of oxalic acid solution (10 mmol L^{−1}).

2.3. PEFC performance tests using cathode catalysts consisting of C functionalized with sulfonate/sulfate group

As the cathode in MEA, functionalized C of HSO₃–C(Norit SX-II) prepared at 353 K (0.49 mmol-H⁺ g^{−1}) and/or 0.1 mL of 5% Nafion dispersion solution (DE521) were mixed with Pt/C (TEC10E50E-HT, Tanaka Precious Metal Industry; 50.8 wt% Pt, mean Pt particle size 4.8 nm). The polymer amount (4.8 mg) contained in the Nafion dispersion solution was essentially equivalent to the amount (5.2 mg) in 0.2 mL Nafion dispersion solution diluted to 2.8% for replica Pt–C (see Section 2.1). The mixing ratios of HSO₃–C, Nafion, and Pt/C were listed in Table 2, entries a–d. The mixture was mounted in an area of 5 cm² on water-repellent C paper (TGP-H-060H, Chemix) and dried.

As the anode in MEA, Pt/C powder on C paper (EC-20-10-7, Electrochem; 20 wt% Pt, mean Pt particle size 4.8 nm) was mixed with 5% Nafion dispersion solution (DE521) and dried. Thus-obtained cathode and anode were set on the each side of 50 μm thick Nafion film (NR212, Dupont), and pressed by applying a pressure of 2 MPa and 393 K for 2 min using a tabletop press (Model SA-302, Tester Sangyo Co.).

PEFC performance tests were performed equipped with the MEA comprising HSO₃–C(Norit SX-II) and Pt/C on the cathode side. Control tests with MEA in which Nafion was used instead of HSO₃–C(Norit SX-II), Nafion was added to HSO₃–C(Norit SX-II), or no addition of proton conductor to Pt/C were also performed. Obtained MEA was set in a PEFC single cell (Model EFC-05-02, Electrochem). O₂ and H₂ gases were flowed at a flow rate of 100 mL min^{−1} to the cathode and anode, respectively, both through water bubbler maintained at 353 K (partial pressure of moisture: 47 kPa).

Impedance measurements were performed for two MEA models to evaluate the effects of sulfonate/sulfate functionalization. On cathode, 20 mg of HSO₃–C(Norit SX-II) or C powder (Norit SX-II)

Table 1
Energy position (eV) and normalized intensity of whiteline peak near the Pt L₃ absorption edge for various Pt–C and the reference samples.

Sample	Energy (eV)	Normalized intensity
(a) Replica Pt–C under air	11,566.7	1.59
(b) Replica Pt–C with 1.5% Nafion and dried	11,566.8	1.28
(c) Replica Pt–C with 2.8% Nafion and dried	11,566.8	1.27
(d) Replica Pt–C in ethanol	11,566.7	1.26
(e) Pt/C(Ketjen black) under air	11,566.5	1.44
(f) Pt/C(Ketjen black) with 1.5% Nafion and dried	11,566.5	1.24
(g) Pt/C(Ketjen black) with 2.8% Nafion and dried	11,566.4	1.23
(h) 5 μm thick Pt metal foil	11,565.6	1.28
(i) PtO ₂	11,567.3	2.07

Table 2

Contents of cathode layer in MEA for PEFC tests.

Entry	Pt/C (mg)	HSO ₃ –C(Norit SX-II) (mg) ^a	Nafion (mg)	Proton content (μmol)
a	9.8	0	0	0
b	9.9	9.7	0	4.8
c	9.9	0	4.8	4.6
d	9.9	4.8	4.8	7.0

^a Prepared at 353 K.

was mounted in an area of 5 cm² on TGP-H-060H. On anode, Pt/C powder (EC-20-10-7) was used in similar manner to the MEA above. The cathode, Nafion film (NR212), and anode were pressed at 2 MPa and 393 K for 2 min using a tabletop press (SA-302). Thus prepared MEA models (effective catalyst area 5 cm²) were sandwiched by two flat copper plates coated with gold with an area of greater than 5 cm². An alternating voltage (10 mV) with the frequency of 10^{–2}–10⁶ Hz was applied to the MEA model and the impedance and phase angle were monitored using a potentiostat/galvanostat (Model VersaSTAT3-500 with an option of frequency response analyzer, Princeton Applied Research).

3. Results

3.1. Whiteline peak intensity near the Pt L₃-edge absorption for Pt samples supported on C

Pt L₃-edge X-ray absorption near-edge structure (XANES) spectra for various Pt–C and the reference samples are depicted in Fig. 1. The whiteline peaks at 11,565–11,567 eV higher than the Pt L₃ absorption edge (11,562 eV for Pt metal) were more intense for replica Pt–C (Fig. 1a and Table 1a) and Pt/C(Ketjen black) (Fig. 1e and Table 1e) under air (1.44–1.59) than 1.28 for Pt metal foil (h). The whiteline peak intensity for replica Pt–C–Nafion (b, c) was 1.28–1.27, weaker than 1.44 for replica Pt–C in air (a). Furthermore, immersed in pure ethanol, the whiteline peak intensity for replica Pt–C (d) decreased to 1.26, that was the smallest intensity among replica Pt–C samples (a–d). Similar trend was observed of the intensity for Pt/C(Ketjen black): 1.44 (under air) > 1.24 (immersed in 1.5% Nafion dispersion solution and dried) > 1.23 (immersed in 2.8% Nafion dispersion solution and dried) (e–g).

3.2. Proton contents in functionalized C with sulfonate/sulfate group

Fig. 2A illustrates the proton contents in HSO₃–C(Norit SX-II) samples as a function of the heating temperature in fuming sulfuric acid during the preparation. The proton content in HSO₃–C(Norit SX-II) samples was maximized by heating at 353 K (0.49 mmol g^{–1}) and rather decreased to 0.38 mmol g^{–1} when the heating temperature further increased to 363 K. One of the reasons of the decrease was that the equilibrium ratio of free SO₃ molecules in gas phase increased above 353 K [13], resulting not to react with C powder anymore. Fig. 2B depicts proton contents in HSO₃–C prepared from several types of C powder. The proton contents in HSO₃–C samples were positively correlated to specific surface area (SA) of precursor C powder, indicating that surface sites to react with SO₃ or H₂SO₄ simply increased as the specific SA grew. The edge of graphene sheet is considered as the reacting site with SO₃ [4].

3.3. PEFC performance using HSO₃–C and/or Nafion with Pt catalysts

Current–voltage characteristics were tested for PEFC using C(Norit SX-II) functionalized with sulfonate/sulfate and/or Nafion

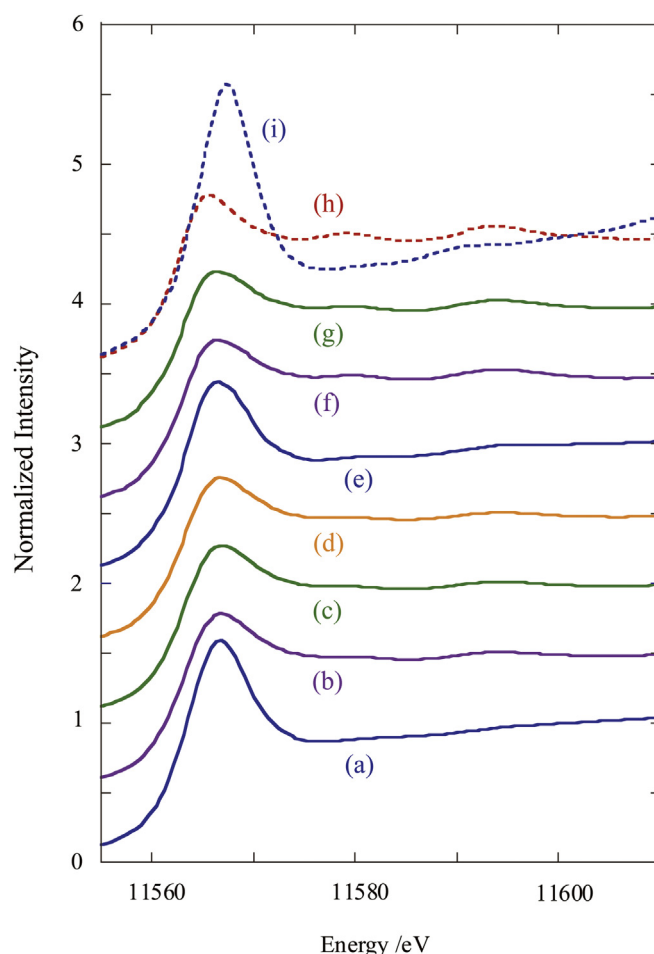


Fig. 1. Pt L₃ absorption edge XANES spectra for replica Pt–C under air (a), replica Pt–C with 1.5% Nafion and dried (b), replica Pt–C with 2.8% Nafion and dried (c), replica Pt–C in ethanol (d), Pt/C(Ketjen black) under air (e), Pt/C(Ketjen black) with 1.5% Nafion and dried (f), Pt/C(Ketjen black) with 2.8% Nafion and dried (g), 5 μm thick Pt metal foil (h), and PtO₂ (i).

(Fig. 3). The cell voltage in entry a in which no proton-conducting functional group/polymer was added to Pt/C catalyst (TEC10E50E-HT; 50.8 wt% of Pt) in cathode (Table 2a) was the lowest and the data values were unstable. This is because the C was water-repellent and the protons were conducted to Pt sites only at an instant when liquid water was in contact with active Pt nanoparticles.

HSO₃–C(Norit SX-II) was mixed with Pt/C in the cathode for entry b (Table 2b). The signal/background ratio in the current–voltage curve was apparently improved compared to data for entry a. It was apparent that HSO₃–C(Norit SX-II) played a role of proton conducting path. However, the cell voltage in entry b was by ~1.6 V lower than that in entry c in which Nafion was used to prepare the cathode Pt/C catalyst instead of mixing HSO₃–C(Norit SX-II) (Table 2c, b).

The current–voltage characteristics were analyzed as a linear fit to the range between 15 and 30 mA cm^{–2} and an extrapolated data of the fit function below the range to current density zero, i.e. voltage axis intercept. The slope evaluated voltage loss dependent on currents and thus should be related to electron and proton conductivity. The voltage axis intercept evaluated overpotential.

The effects of sulfonate/sulfate functionalization were compared to that of Nafion by fixing the proton content (4.6–4.8 μmol) in cathode catalysts (Table 2, entries b and c). The slope for entry b

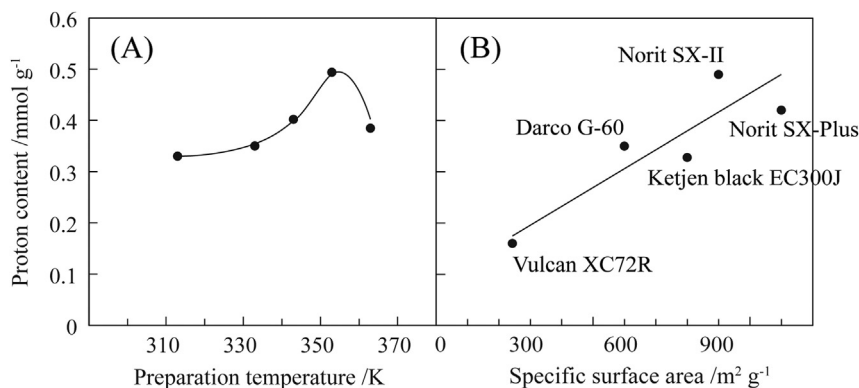


Fig. 2. Proton contents in $\text{HSO}_3\text{-C}$ as a function of preparation temperature in the range of 313–363 K using C black (Norit SX-II) precursor (A) and as a function of specific SA of various precursor C powders at fixed preparation temperature of 353 K (B).

($-2.4 \text{ V mA}^{-1} \text{ cm}^2$) was equivalent or more flat than the one for entry c ($-2.7 \text{ V mA}^{-1} \text{ cm}^2$), but the voltage axis intercept in entry b (0.69 V) was apparently smaller than the one for entry c (0.85 V). Therefore, $\text{HSO}_3\text{-C(Norit SX-II)}$ exhibited comparable or slightly better proton conductivity compared to Nafion, but the over-potential was by 0.16 V higher than that using Nafion.

In the entry d, both $\text{HSO}_3\text{-C(Norit SX-II)}$ and Nafion were mixed to prepare the cathode (Table 2d). When 9.7 mg of $\text{HSO}_3\text{-C}$ was added to 9.9 mg of Pt/C with Nafion, the amount of Nafion suspension solution seemed insufficient to mix well with totally 20 mg of powder. Instead, the amount of $\text{HSO}_3\text{-C}$ for mix was reduced to a half in entry d. The slope was most flat ($-2.1 \text{ V mA}^{-1} \text{ cm}^2$) among all tests in Fig. 3 and the voltage-axis intercept value was as high as 0.86 V. This was the optimized cathode catalyst in which the boundary between C for the electron conduction and proton-conducting polymer was maximized by functionalizing the C surface by sulfonate/sulfate groups. The current–voltage characteristics for entries c and d were stable and reproducible in repeated MEA performance tests.

In Bode plot based on the impedance measurements (Fig. 4A), the impedance for MEA model comprising $\text{HSO}_3\text{-C(Norit SX-II)}$ was $2.4 \times 10^3 \Omega$ versus $14.2 \times 10^3 \Omega$ for MEA model comprising C(Norit SX-II) at 10^{-2} Hz . This impedance difference was a general trend in all the frequency range, suggesting the greater proton conductivity when C surface was functionalized with sulfonate/sulfate. This

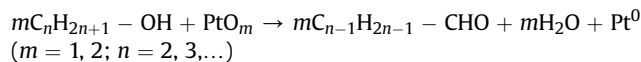
trend was also supported in Cole–Cole plot (Fig. 4B). The (part of) impedance circle for MEA model comprising $\text{HSO}_3\text{-C(Norit SX-II)}$ was apparently smaller than that for MEA model comprising C(Norit SX-II), suggesting smaller impedance (greater proton conductivity) for MEA model comprising $\text{HSO}_3\text{-C(Norit SX-II)}$.

4. Discussion

4.1. Correlation between platinum electronic state and Nafion coverage

The changes of whiteline peak intensity that appeared at 11,565–11,567 eV higher than the Pt L_3 absorption edge were explained due to the change of oxidation states of Pt sites by forming the boundary between Pt nanoparticles and Nafion (Fig. 5). Under air, the valence of surface Pt sites was the mixture of 4+, 2+, and 0 (Fig. 5A) [14]. Similar oxidation/reduction trends of surface sites were monitored based on peaks near the X-ray absorption edges of V, Cu, and Sn K and Au and Pb L_3 [15–22].

Next, the oxidic surface Pt sites were reduced to Pt^0 when the Pt–C catalyst was immersed in Nafion dispersion solution (Fig. 5B). The reduction was found by the reaction not with Nafion but with alcohol(s). 14–26% of 1-propanol and 46–72% of ethanol were contained in Nafion dispersion solution used (2.8–1.5%). The Pt sites in replica Pt–C sample were totally reduced to Pt^0 in a blank test by just immersed in ethanol based on the whiteline intensity became smaller (1.26) to essentially the same as that for Pt metal (1.28; Table 1d, h). This seems not only the reduction of surface Pt sites but (nearly) total reduction of 2.0–4.5 nm of Pt nanoparticle bulk based on the peak intensity changes via the following reaction.



Please note that most of Pt sites of replica Pt–C immersed in ethanol were reduced (Table 1d) whereas they were re-oxidized to Pt^{2+} and/or Pt^{4+} upon exposed to air based on Pt L_3 XANES. In clear contrast, negligible re-oxidation of Pt^0 was detected when Nafion dispersion solution was used in Pt L_3 XANES (Table 1b, c, f, g) probably because Nafion totally covered Pt nanoparticles for the dried replica Pt–C and Pt/C (Ketjen black) samples. Although similar amount of Nafion was used on the cathode in the MEA performance tests (Fig. 3) to that for X-ray study (Fig. 1), but the in-situ environment of Pt nanoparticle surface was not exactly identical with the one for dried samples of Table 1b, c, f and g because the electrodes during the MEA performance tests were surrounded by pseudo-liquid Nafion aqueous solution.

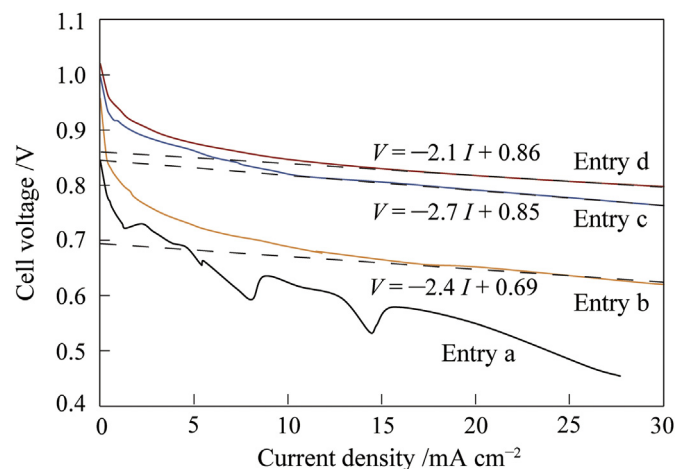


Fig. 3. Current–voltage characteristics in MEA performance test. Entry a (black), entry b (orange), entry c (blue), and entry d (red). The dotted lines are the fit in the region between 15 and 30 mA cm^{-2} and the lines were extrapolated to the V-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

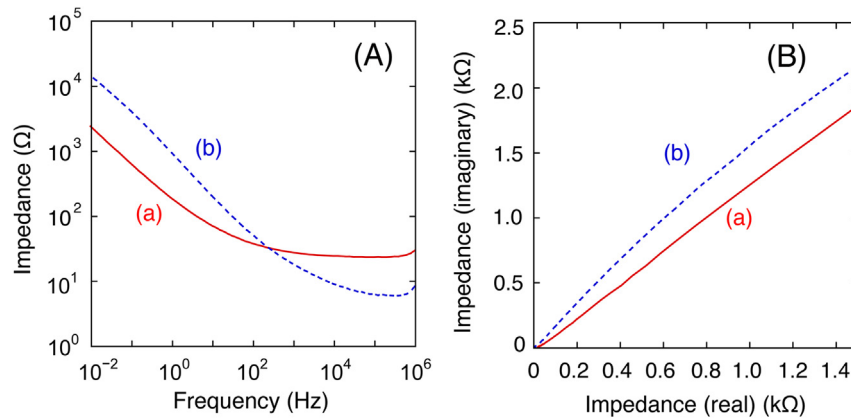


Fig. 4. Bode plot (A) and Cole–Cole plot (B) based on impedance measurements for MEA model using $\text{HSO}_3\text{-C(Norit SX-II)}$ (a; solid line) and C(Norit SX-II) (b; dotted line) as cathode. Common Pt/C powder (EC-20-10-7) was used as anode.

The reason why the Pt–C(Ketjen black) was more effectively reduced to Pt^0 was considered compared to replica Pt–C once immersed in reductive medium (Table 1). The major reason is that the Pt nanoparticles were more surrounded by C atoms synthesized from ethyne gas decomposed over Pt for replica Pt–C and thus the interface Pt sites with C cannot contact with Nafion/alcohol. The interface between Pt and C for replica Pt–C was extensively investigated by state-sensitive Pt $L_{3\text{-edge}}$ XAFS spectroscopy [8].

When the samples immersed in 2.8–1.5% Nafion dispersion solution were dried (Table 1b, c, f, g), a part of Pt surface protected with Nafion thin film remained as Pt^0 and the other part of Pt surface in direct contact with air was re-oxidized to Pt^{2+} and Pt^{4+} (Fig. 5C). In summary, Pt L_3 whiteness peak intensity for Pt–C catalysts in contact with Nafion was a sensitive indicator of the Nafion coverage over the Pt surface and thus also the formation of the boundary between Nafion and Pt surface sites.

4.2. Efficiency of proton conduction for $\text{HSO}_3\text{-C}$ and Nafion

Surface-functionalized $\text{HSO}_3\text{-C(Norit SX-II)}$ was an effective proton conductor to reduce the voltage loss at cathode in the PEFC performance tests (Fig. 3a, b). Furthermore, impedance

measurements for model MEA samples supported improved proton conductance due to the C surface functionalization by sulfonate/sulfate in comparison to bare C black (Fig. 4a, b).

A proton conduction model in cathode is proposed (Graphical abstract, right). Using Nafion to prepare the cathode catalyst layer (Fig. 3c), protons would diffuse by hopping via sulfonate groups of Nafion. Using $\text{HSO}_3\text{-C(Norit SX-II)}$ in cathode (Fig. 3b), protons would diffuse also by hopping via sulfonate/sulfate groups of functionalized C. The proton conductivity via $\text{HSO}_3\text{-C(Norit SX-II)}$ was comparable or slightly superior to via Nafion, but apparently extra energy was required for the proton conduction via $\text{HSO}_3\text{-C(Norit SX-II)}$ based on the evaluation of overpotential as the voltage-axis intercept values (Fig. 3b, c). One of the reasons was that the sulfonates of Nafion are neighboring bonded to strong electron withdrawing CF_2 group and would exhibit in strong acid character in contrast that functionalized sulfonate/sulfates bound to C surface should be less acidic for $\text{HSO}_3\text{-C(Norit SX-II)}$ [23]. Therefore, protons in more acidic medium, i.e. Nafion, were more mobile and leading to smaller overpotential compared to in $\text{HSO}_3\text{-C}$.

The major proton conduction path should be via the sulfonates of Nafion in both cases. However, the proton conduction path will

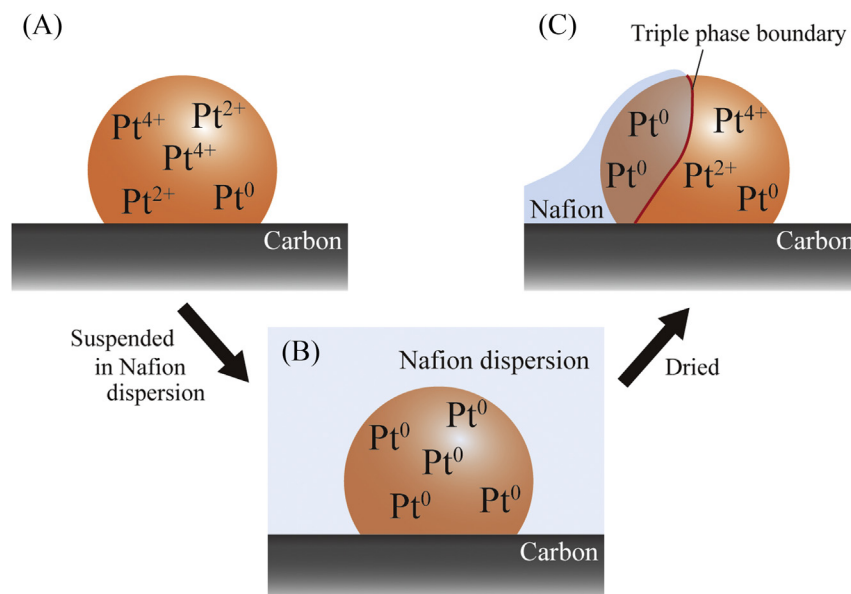


Fig. 5. Reduction and oxidation of surface Pt sites in Pt–C catalyst with Nafion. Pt was oxidized under air (A), reduced by alcohol in disperse medium (B), and partially re-oxidized under air (C).

be widened by the presence of sulfonate/sulfates of $\text{HSO}_3\text{--C}$ (Norit SX-II) in addition to Nafion as compared to the interface with Nafion only (Graphical abstract, right) as demonstrated in Fig. 5d. Further optimization with respect to triple phase boundary will be expected by functionalizing the C black surface with CF_2 -branched sulfonates $(\text{CF}_2)_n\text{--SO}_3\text{H}$ in which equivalent strong acid sites are expected to the side branches of Nafion.

5. Conclusions

It was possible to evaluate the boundary between proton conducting polymer and surface Pt sites based on the synchrotron X-ray monitoring of Pt valence state change dependent on the amounts and concentrations of Nafion dispersion solutions used. Moreover, the support C was functionalized by sulfonate/sulfates to conduct protons as demonstrated in MEA performance tests and impedance measurements.

Acknowledgments

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References

[1] E. Antolini, J. Appl. Electrochem. 34 (2004) 563–576.

- [2] W.K. Epting, J. Gelb, S. Litster, Adv. Funct. Mater. 22 (2012) 555–560.
- [3] D. Friebe, D.J. Miller, C.P. O'Grady, T. Anniyev, J. Bargar, U. Bergmann, H. Ogasawara, K.T. Wikfeldt, L.G.M. Pettersson, A. Nilsson, Phys. Chem. Chem. Phys. 13 (2011) 262–266.
- [4] K. Nakajima, M. Hara, ACS Catal. 2 (2012) 1296–1304.
- [5] Q. Shu, J. Gao, Z. Nawaz, Y. Liao, D. Wang, J. Wang, Appl. Energy 87 (2010) 2589–2596.
- [6] S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, M. Hara, J. Am. Chem. Soc. 130 (2008) 12787–12793.
- [7] X. Mo, D.E. López, K. Suwannakarn, Y. Liu, E. Lotero, J.G. Goodwin Jr., C. Lu, J. Catal. 254 (2008) 332–338.
- [8] K. Oka, Y. Shibata, T. Itoi, Y. Izumi, J. Phys. Chem. C 114 (2010) 1260–1267.
- [9] J.H. Nam, Y.Y. Jang, Y.U. Kwon, J.D. Nam, Electrochem. Commun. 6 (2004) 737–741.
- [10] F. Li, K.Y. Chan, H. Yung, C. Yang, S.W. Ting, Phys. Chem. Chem. Phys. 15 (2013) 13570–13577.
- [11] Y. Izumi, T. Itoi, S. Peng, K. Oka, Y. Shibata, J. Phys. Chem. C 113 (2009) 6706–6718.
- [12] M. Vaarkamp, H. Linders, D. Koningsberger, XDAP Version 2.2.7, XAFS Services International, Woudenberg, The Netherlands, 2006. <http://www.xsi.nl>.
- [13] J. Schrage, Fluid Phase Equilib. 68 (1991) 229–245.
- [14] Y.C. Chiang, J.R. Ciou, Int. J. Hydrogen Energy 36 (2011) 6826–6831.
- [15] Y. Izumi, K. Konishi, D. Obaid, T. Miyajima, H. Yoshitake, Anal. Chem. 79 (2007) 6933–6940.
- [16] Y. Izumi, H. Nagamori, F. Kiyotaki, D. Masih, T. Minato, E. Roisin, J.P. Candy, H. Tanida, T. Uruga, Anal. Chem. 77 (2005) 6969–6975.
- [17] M. Morikawa, N. Ahmed, Y. Yoshida, Y. Izumi, Appl. Catal. B 144 (2014) 561–569.
- [18] Y. Yoshida, Y. Mitani, T. Itoi, Y. Izumi, J. Catal. 287 (2012) 190–202.
- [19] Y. Izumi, D. Obaid, K. Konishi, D. Masih, M. Takagaki, Y. Terada, H. Tanida, T. Uruga, Inorg. Chim. Acta 361 (2008) 1149–1156.
- [20] Y. Izumi, F. Kiyotaki, T. Minato, Y. Seida, Anal. Chem. 74 (2002) 3819–3823.
- [21] Y. Izumi, F. Kiyotaki, H. Nagamori, T. Minato, J. Electron Spectrosc. Relat. Phenom. 119 (2001) 193–199.
- [22] H. Oyanagi, M. Ishii, C.H. Lee, N.L. Saini, Y. Kuwabara, A. Saito, Y. Izumi, H. Hashimoto, J. Synchrotron Radiat. 6 (1999) 155–157.
- [23] D.A. Evans, The Evans Group Website, Evans pK_a Table, November 8, 2013. http://evans.harvard.edu/pdf/evans_pKa_table.pdf.